

# GENESIS OF AUGITE-BEARING UREILITES: EVIDENCE FROM LA-ICP-MS ANALYSES OF PYROXENES AND OLIVINE. J. S. Herrin<sup>1</sup>, C-T. A. Lee<sup>2</sup>, D. W. Mittlefehldt<sup>1</sup>, and H. Downes<sup>3</sup>,

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**Introduction:** Ureilites are ultramafic achondrites composed primarily of coarse-grained low-Ca pyroxene and olivine with interstitial carbonaceous material, but a number of them contain augite [1]. Ureilites are considered to be restites after partial melting of a chondritic precursor, although at least some augite-bearing ureilites may be partially cumulate [1, 2]. In this scenario, the augite is a cumulus phase derived from a melt that infiltrated a restite composed of typical ureilite material (olivine+low-Ca pyroxene) [2]. To test this hypothesis, we examined the major and trace element compositions of silicate minerals in select augite-bearing ureilites with differing mg#.

Polished thick sections of the augite-bearing ureilites ALH 84136, EET 87511, EET 96293, LEW 88201, and META78008 and augite-free ‘typical’ ureilite EET 90019 were examined by EPMA for major and minor elements and laser ablation ICP-MS (LA-ICP-MS) for trace elements, REE in particular. Although EET 87511 is reported to contain augite, the polished section that we obtained did not.

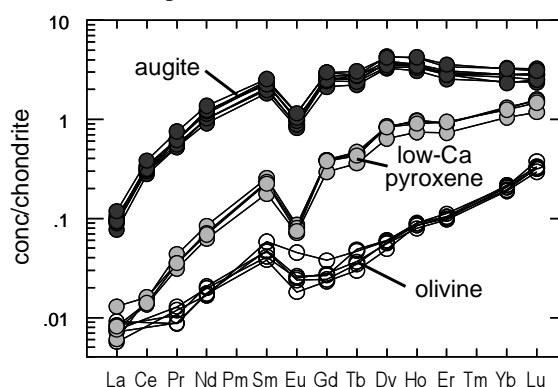
**Results:** Core mg#'s of ferromagnesian silicate minerals are uniform within a given ureilite, but vary substantially between different meteorites [1]. In those we examined we found a range of core olivine mg# from 77 in the most ferroan sample (META78008) to 97 in ALH 84136. Like augite-bearing ureilite Hughes 009 [2], olivine from EET 96293 plots off Fe/Mn vs. Fe/Mg ureilite trend [3]. The average composition of low-Ca pyroxenes was ~Wo<sub>5</sub> in all samples with the exception of the non-augite bearing EET 90019 which was Wo<sub>9</sub>. Trace elements including REE were measured in olivine, low-Ca pyroxene, and augite by LA-ICP-MS. In all cases these minerals were strongly LREE depleted with prominent negative Eu anomalies (Fig. 1). The lowest concentrations were found for LREE in olivines and for these elements analytical uncertainty was <20% with the exception of Ce, with nearly all other measurements having lower uncertainty.

**Discussion:** Bulk REE analyses of ureilites are often difficult to interpret due to the effects of contamination [4], to which ureilites are particularly susceptible due to their low REE contents. The observed “V-shaped” REE distributions are attributed to terrestrial contamination [4] or late addition of an indigenous LREE-rich fluid [5]. *In situ* analysis of mineral grain interiors is preferred over both bulk and mineral separation

analyses because it avoids the influence of surface contaminants and grain boundary partitioning effects. Moreover, mineral and melt inclusions can be avoided both by optical control of sampling locations and inspection of time-resolved analysis signals to eliminate spikes in signal associated with inclusions.

At first glance, the observed REE patterns are consistent with a restitic origin derived from a chondritic precursor by extraction of basaltic melt. Indeed, this simplified genetic history gives a first-order description of the formation of all known typical ureilites. Clues to the formation of augite-bearing ureilites are found in REE disequilibrium between different phases.

Lee et al. [6] used lattice strain theory to predict mineral/mineral partitioning of REE in terrestrial peridotites, and compared these predictions to analyses. For a system in equilibrium, the relative concentrations of REE should vary systematically as a function of ionic radius. In a restite of equilibrium melting we should expect equilibrium distribution of REE to prevail. Deviations in natural samples can indicate non-equilibrium melting processes or later addition without equilibration. In this study we apply this same logic to ureilites, whose genetic history is analogous to harzburgitic terrestrial mantle in that mineral/mineral REE equilibrium should have been largely established with sustained high temperatures during and after silicate melt depletion.



**Figure 1.** Chondrite-normalized REE content of mafic phases in augite-bearing ureilite EET 96293 showing typical relative concentrations of REE between different phases, LREE depletion, and negative Eu.

In the ureilites we examined we observed systematic variation through the HREE and MREE consistent with predictions from lattice strain theory, demonstrating chemical equilibrium between phases for

these elements. Some of the samples, however, exhibit pronounced LREE disequilibrium, as demonstrated by the upward concave parabolic distribution in Figs. 2, 3. We propose that such an effect is consistent with infiltration of silicate melts into a restite as hypothesized [2]. It is also consistent with reaction of a cumulate with a final differentiate melt, perhaps being mobilized from elsewhere in the system by filter pressing.

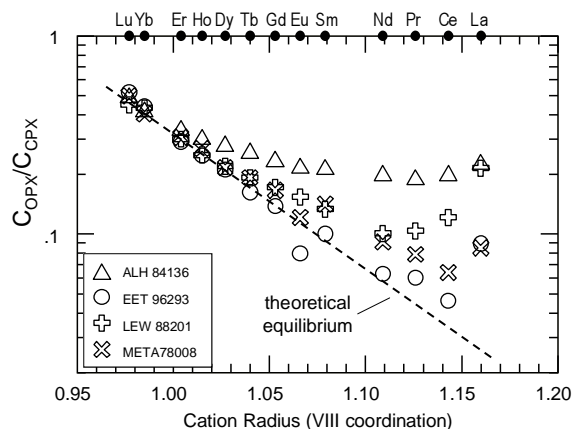
Since REE are incompatible they become enriched in the melts, especially as melts differentiate. Moreover, since LREE are the most incompatible they are the most concentrated in the melt phase. Interaction between solid minerals and a melt will have the greatest effect on the LREE composition of the minerals. In a restite, concentrations of REE decrease in the order clinopyroxene - low-Ca pyroxene - olivine. It follows then that a disequilibrium process that would add REE, especially LREE, to a restite would affect these phases in the reverse order so that  $C_{OL}/C_{OPX}$ ,  $C_{OL}/C_{CPX}$ , and  $C_{OPX}/C_{CPX}$  (where  $C_{OPX}$  refers to the concentration of an element in low-Ca pyroxene) would all be higher than expected. In the case of augite-bearing ureilites, the clinopyroxene is thought to be a cumulus phase derived from the melt, and not part of the original restite [2], but the order above should still apply.

If high temperature is maintained for a long enough time, this effect will eventually disappear as mineral phases once again reach equilibrium. In these ureilites the system must have cooled below diffusive exchange temperatures before this could occur. We observe a general increase in  $C_{OL}/C_{OPX}$  for LREE with increasing temperatures calculated from the pigeonite thermometer of [7] (Fig. 4), but this is counter-intuitive. At higher T, diffusive exchange should be more rapid and we would have predicted a decrease in  $C_{OL}/C_{OPX}$  with increasing T. Diffusion coefficients for most elements are higher for olivine than pyroxene and closure temperatures lower [8]. One explanation may be that LREE from the melt diffused more rapidly into olivine than low-Ca pyroxene, and that this rate difference increased with T and continued to lower T. ALH 84136 is an exception to the above trend in that it has the highest calculated T, but one of the lowest partitioning ratios.

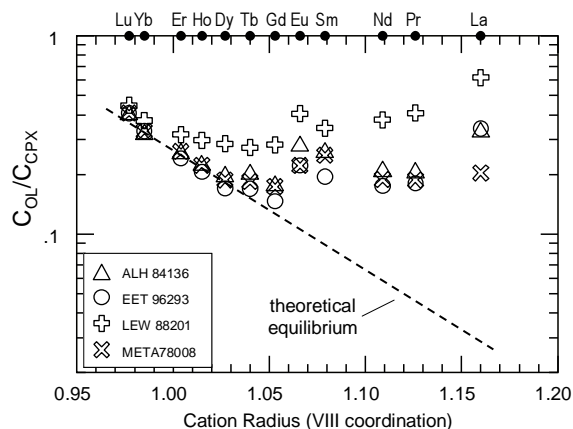
**Conclusions:** Relative abundances of REE in mafic minerals of augite-bearing ureilites indicate a history of basalt depletion from a chondritic precursor, as is typical of ureilites. Variations in the relative abundances of REE between phases demonstrate disequilibrium between phases, a possible indication of either melt infiltration to the restite or else reaction of a cu-

mulate with late differentiate melt as a possible mechanism for formation of augite-bearing ureilites.

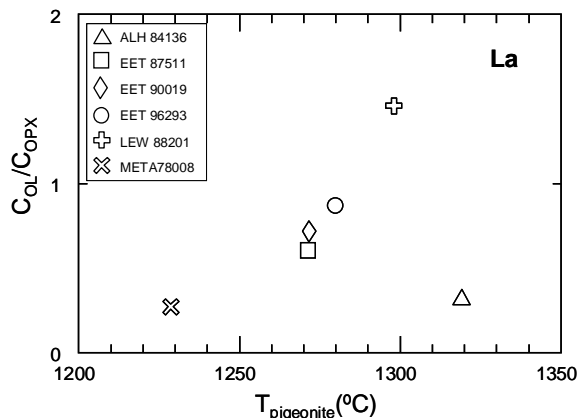
**References:** [1] Mittlefehldt D. W. *et al.* (1998) *Rev. Mineral.*, 36, ch. 4. [2] Goodrich C. A. *et al.* (2001) *GCA*, 65, 621-652. [3] Goodrich C. A. *et al.* (2004) *Che. Erde Geochem.*, 64, 283-327. [4] Guan Y. and Crozaz G. (2000) *MAPS*, 35, 131-144. [5] Boynton W. V. *et al.* (1976) *GCA*, 40, 1439-1447. [6] Lee C. A. *et al.* (2007) *GCA*, 71, 481-496. [7] Singletary S. J. and Grove T. L. (2003) *MAPS*, 38, 95-108. [8] Ganguly J. *et al.* (2007) *GCA*, 71, 3915-3925.



**Figure 2.** Relative concentrations of REE between low-Ca pyroxene and augite as a function of ionic radius.



**Figure 3.** Relative concentrations of REE between olivine and augite as a function of ionic radius. Eu is anomalous because much may be divalent in these reduced rocks.



**Figure 3.** Estimated pigeonite equilibration T vs. average concentration of La (LREE) in olivine relative to low-Ca pyroxene.